UNIVERSITI PUTRA MALAYSIA

DETERMINING FRYING OIL DETERIORATION USING CHEMICAL AND PHYSICAL METHODS

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By

FRAGE LHADI FRAGE ABOOKLEESH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for Master of Science

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DEDICATION

This work is dedicated to my parents and my wife.

Abstract of the thesis presented to the senate of Universiti Putra Malaysia in fulfilment of the requirement for Degree of Master of Science

DETERMINING FRYING OIL DETERIORATION USING CHEMICAL AND PHYSICAL METHODS

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FRAGE LHADI FRAGE ABOOKLEESH

July 2009

Chairman: Abdulkarim Sabo Mohammed, PhD

Faculty: Food Science and Technology

This research was performed to assess the oil deterioration during deep fat frying. It was also conducted to compare and correlate oil quality parameters namely, total polar compound (TPC), free fatty acids (FFA), peroxide value (PV), P-Anisidine value (p-AV), specific extinction ($E^{1\%}_{1cm}$233, 269nm), iodine value (IV), flavor, color, viscosity, with changes in the heating profile of melting point, and investigate changes in the properties of oils with different kinds of food during deep-fat frying of chicken, banana and sweet potato. The frying oil consisted of five types of commercial oils, namely, canola, corn, soybean, sunflower and palm olein. These oils were used to fry, banana, sweet potato and chicken at 185±5°C for 6 hr per day for sixe days until the total time of 30 hours with an interval time of 20 min. One and half kilograms of each oil sample to be tasted and 100g of each fried product was used for the frying. The frying time was set for 7 minute for banana and sweet potato and 15 minute for chicken. Each day, fresh oil was added to replenish the oil used. Oils used were withdrawn on the following day and before starting the next frying

cycle and was kept in the freezer at -20C°. The oils were analyzed for PV, IV, p-AV, FFA, $E^{1\%}_{1cm}$233, 269nm, TPC, color, viscosity, flavor (by zNose) and thermal behavior (melting point by DSC).

In this study, DSC was used to monitor the deterioration of frying oils during deep fat frying based on qualitative investigation of the thermal behavior (melting point). The investigation began with the successful comparison of the DSC thermal curves of five different vegetable oils. The heating thermogram for the oils showed varying degree of changes especially in the last melting peak position during the course of frying. The heating thermogram showed that there is one major peak and two small shoulders peaks and used the offset of last melting peak; ("the last order peak of the DSC heating thermogram was used to represent the changes in melting point"). Flavor analysis is typically performed by a qualitative analysis of zNose chromatogram. A novel approach using a surface acoustic wave (SAW) sensing based electronic nose for favor analysis was used in this study for detecting the losing of volatile compound in vegetables oils. A statistical correlation was carried out on the DSC heating thermogram with standard chemical and physical methods. Significant linear relationship was found between melting point, TPC, IV, $E^{1\%}_{1cm}$233, 269nm and viscosity. The DSC heating thermogram showed excellent correlation ($P<0.05$) with the standard chemical analysis.

The finding of this study reveals that palm olein showed significantly ($P<0.05$) lower in all measured parameters than the other oils used. The extent of oil deterioration was best reflected in the changes in percent TPC, IV, $E^{1\%}_{cm}$ at 233nm..

Abstrak tesis yang akan dibentangkan kepada Senat Universiti Putra Malaysia sebagi memenuhi keperluan untuk Ijazah Master Sains

Penentuan Tahap Kemerosotan Minyak Masak Menggunakan Kaedah Kimia dan Fizikal.

Oleh

FRAGE LHADI FRAGE ABOOKLEESH

Julai 2009

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Fakulti: Sains dan Teknologi Makanan

Kajian ini dijalankan untuk menilai kemerosotan kualiti minyak masak semasa mengggoreng. Ia juga dijalankan untuk membuat perbandingan dan hubung kait antara parameter kualiti minyak iaitu, total sebatian polar (TPC), asid lemak bebas (FFA), nilai peroksida (PV), nilai P-Anisidine (P-AV), 'specific extinction' ($E^{1\%}_{1cm}$233, 269nm), nilai iodin (IV), aroma, warna, kepekatan dengan perubahan profil kepanasan dalam takat lebur dan seterusnya mengenalpasti perubahan ciri-ciri minyak semasa menggoreng ayam, pisang dan keledek. Minyak masak terdiri daripada lima jenis minyak komersil iaitu minyak canola, minyak jagung, minyak kacang soya, minyak biji bunga matahari dan minyak olein kelapa sawit. Minyak-minyak tersebut digunakan untuk menggoreng tiga jenis produk iaitu pisang, keledek dan ayam pada suhu 185±5°C selama 6 jam sehari sehingga total masa 30 jam

dengan masa perantara selama 20 minit. Satu setengah kilogram daripada setiap jenis sampel minyak dan 100g daripada setiap produk telah digunakan semasa memasak. Kadar masa menggoreng telah ditetapkan selama 7 minit untuk pisang dan keledek, manakala 15 minit untuk ayam. Pada setiap hari, minyak masak baru telah ditambah untuk menggantikan minyak masak yang telah digunakan. Minyak yang telah digunakan telah diambil pada hari tersebut dan juga sebelum proses penggorengan yang seterusnya, kemudian ia disimpan di dalam peti ais pada suhu -20 C^{o} untuk analisis nilai PV, IV, p-AV, FFA, $E^{1\%}_{cm}$ pada 233nm dan 269nm, TPC, warna, kepekatan, aroma (menggunakan zNose™) dan sifat termal (takat peleburan menggunakan DSC).

Dalam kajian ini juga, DSC digunakan untuk melihat kemerosotan kualiti pada minyak masak semasa menggoreng berdasarkan pemerhatian kualitatif sifat termal (takat peleburan). Pemerhatian ini bermula dengan keberhasilan perbandingan garis lengkuk termal DSC pada lima jenis minyak masak tersebut. Thermogram pemanasan untuk kesemua minyak menunjukkan kepelbagaian darjah perubahan terutamanya pada kedudukan puncak takat lebur yang terakhir semasa menggoreng. Thermogram pemanasan menunjukkan satu puncak utama dan dua puncak kecil. Suhu bagi takat lebur ditentukan dengan menggunakan puncak peleburan yang terakhir (susunan puncak terakhir dalam thermogram DSC digunakan untuk mewakili perubahan takat lebur). Analisis kualitatif aroma ditunjukkan dengan menggunakan kromatogram zNose™. Pendekatan baru menggunakan sentuhan 'surface acoustic wave' (SAW) berdasarkan 'electronic nose' untuk analisis aroma diaplikasikan dalam kajian ini untuk mengenalpasti perubahan sebatian meruap di dalam minyak sayuran. Hubungkait statistik telah dilakukan antara

thermogram pemanasan DSC dengan kaedah kimia dan fizikal mengikut piawai. Hubungan linear yang signifikasi telah diperolehi antara takat lebur, TPC, IV, $E^{1\%}_{1cm}233$, 269nm dan kepekatan. Thermogram pemanasan DSC menunjukkan korelasi yang terbaik ($P<0.05$) dengan analisis kimia piawai.

Penemuan kajian ini membuktikan minyak olein kelapa sawit menunjukkan signifikasi ($P<0.05$) yang rendah dalam semua parameter yang diukur berbanding dengan minyak lain yang digunakan. Kelewatan terhadap kemerosotan nilai minyak dihubungkan dengan baik dalam perubahan peratusan dalam TPC, IV, $E^{1\%}_{cm}$ pada 233nm dan 269nm, kepekatan, dan takat lebur di dalam semua jenis minyak yang digunakan.

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I certify that a Thesis Examination Committee has met on 17 July 2009 to conduct the final examination of Frage Lhad Frage Abookleesh on his thesis entitled "Determining Frying Oil Deterioration Using Chemical and Physical Methods" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory committee were as follows:

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Date: 16 October 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

Frage Lhadi Frage Abookleesh

Date: 12 August 2009

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

General Introduction

Fats and oils are constructed of building blocks called "triacylglycerol" resulting from the combination of one unit of glycerol and three units of fatty acids. They are insoluble in water but soluble in most organic solvents (Harwood, 2000). Fats and oils play important functional and sensory roles in food products. They are responsible for carrying, enhancing, and releasing the flavor of other ingredients as well as for interacting with other ingredients to develop the texture and mouthfeel characteristics of fried foods. In addition, fats and oils are sources of energy (providing 9 kcal/g, more than twice that supplied by proteins or carbohydrates), fat-soluble vitamins (A, D, E, and K), and the essentials linoleic and linolenic acids responsible for growth (Rossan *et al.*, 1999). Oils and fats occur naturally in many of our foods, such as dairy products, meats, poultry, nuts, fish, and vegetable oil seeds. They are very important in the processing of many favorite foods. Examples include French fried potatoes, salad dressings, an infinite variety of breads and rolls, and dessert items (Lawson, 1995).

Vegetable fats and oils are widely used in the food, pharmaceutical, cosmetic and chemical industries and are normally obtained from oilseeds such as sesame seed, soybean, and cotton seed oil. Among these fat and oil sources, cocoa butter (CB) is highly appreciated because of its physical and chemical characteristics (Solis and Duran,

2004; Edward and Michael, 1996). More than 95% of fats and oils consist of triacylglycerol. The type and location of the fatty acids on the glycerol backbone define the physical and chemical characteristics of the various fats (Lawson, 1995). Fatty acids may be either saturated or unsaturated. There are many types of oils and fats available for frying. Until 1986, fats of animal origin were the primary fats used by the food service. The food industry tended to use animal/vegetable blends as well as partially hydrogenated vegetable oils (Lawson,1995). The vegetable oils used include soybean, cottonseed, corn, peanut, olive, canola, safflower, sunflower, soybean, and canola oils which are always partially hydrogenated before being used for frying to increase its stability. Cottonseed, corn, peanut, and olive oils are used as a stable source of polyunsaturated fatty acids because of their low linolenic acid content (O'Berin., 1998a).

Deep-fat frying of food is considered everywhere in the world to be the most common unit operation used in food preparation. Therefore, to produce, preserve, and market fried food optimally, it is important to understand the frying mechanism (Rossan *et al.*, 1999). Nowadays, deep-fat frying and microwave heating are two of the most commonly used procedures for preparation and manufacture of foods throughout the world. The general advantages of deep-fat frying are that heat destroys bacteria and toxins, and also makes fried food more palatable and, therefore, readily accepted by the consumer (Tan and Che Man, 2002). During frying, a number of reactions occur in the frying oil causing oxidative and hydrolytic degradation and polymerization of the oil. Heat, water, air and the presence of contaminating materials together with the duration of frying

cause these degradative reactions. The main causes of oil degradation are oxidation, thermal treatment, and oil food interaction at high temperature (Gary, *et al.,* 1996). Oxidative and chemical changes in frying fats during use are characterized by a decrease in the total unsaturation of the fat with increase in free fatty acids, foaming, color, and viscosity, and polar and polymeric materials (Min and Lee, 1996). The quality of the oil used in deep-fat frying contributes to the quality of the fried food. The oil or fat used in the frying operation becomes part of the food we eat and is, of course, the major factor in the quality and nutritional value of the food we eat (Rossell,2001). In addition, highly oxidized oils may also produce polycyclic aromatic hydrocarbons that are known as carcinogens. As these reactions precede, the quality of oil changes and may eventually reach a point where it is no longer possible to prepare high-quality fried products and the frying oil will have to be discarded (Stevenson *et al.* 1984; Sebedio *et al.* 1990; Romero *et al.* 1998).

The chemistry of oils and fats at frying temperature is rather complex. More than 500 different chemical compounds have been detected as a result of oxidation, polymerization and hydrolysis. The type of product used in frying and the time of frying are two important factors affecting the quality of oil. Many works have recommended that further studies should be done on the effect of different products on oil quality, yet not many studies have been carried out in this context (Gandel *et al.,* 1996).

The problem statements considered in carrying out this research are as follows:

(1) Deep fat frying causes variety of oxidative products, that changes oil quality.

(2) Changes in oil quality during deep fat frying also affects the quality of the fried product.

(3) Some of the oxidative, hydrolytic and polymer products produced during deep fat frying are toxic and potentially hazardous to human health.

Due to the above problem and in view of the following:

A. The need for the development of a rapid technique to ascertain the level of frying fat deterioration for quality assurance purposes

B. The need to estimate how different oils affect the quality of the product fried in it and to what extent does the fried product affect the quality of the oil used

C. To estimate the level of deterioration of the oil that poses risk to the health of the consumer,

The main aim of this study was to assess the quality changes of some selected vegetable oils during deep fat frying of banana, sweet potato and chicken using physico-chemical methods.

The specific objectives of the study are as follows:

(1) To evaluate some of the important chemical and physical changes of the selected vegetable oils during frying.

(2) To study the affect of different types of food on the frying oil quality.

(3) To develop a technique to measure oil deterioration based on changes in heating thermal profile of the used oils using Differential Scanning Calorimetry.

CHAPTER 2

Literature review

Vegetable oils and fats

Vegetable oils and fats make up one of three major classes of food materials, the others being carbohydrates, and proteins. Fats and oils have been known since ancient times as they were easily isolated from their source (Wiess, 1970). The largest sources of vegetable oil at present are the seeds of annual plants such as soybean, cottonseed, peanut, sunflower, safflower, corn, palm olein and canola or rapeseed (Weiss, 1970). Acylglycerols belong to a large group of natural organic polar compounds known as lipids, which includes the waxes, lecithins and phospholipids. These are widely distributed in foods and are of great nutritional value. Fats provide fatty acids which are necessary to animal metabolism and represent a concentrated reserve of energy, yielding about 37 KJ, per gram (Harwood, 2000). The great nutritional importance of oils and fats in feeding the ever increasing world population, and the technological advances have led to higher production levels and improvements in product quality and versatility of these commodities during the last two decades (Salunkhe *et al.,* 1992). The fats found in foods are essential to our diet. Fats supply the body with energy and essential fatty acids, promote the absorption of fat-soluble vitamins and provide insulation. Dietary reference intakes, issued by the Institute of Medicine (IOM) of the National Academies in 2002, recommend a range of 20 to 35 percent of total calories from fat to meet the